

Eclética Química

Print version ISSN 0100-4670 *On-line version* ISSN 1678-4618

Eclet. Quím. vol.22 São Paulo 1997

<http://dx.doi.org/10.1590/S0100-46701997000100008>

Electron transfer by singlet excited state of porphyn and electron acceptor affinity in rigid medium: photoacoustic phase angle analysis

Marinônio Lopes CORNÉLIO*

ABSTRACT: Photoacoustic spectroscopy provides information about both amplitude and phase of the response of a system to an optical excitation process. This paper presents the studies of the phase in the electron transfer process between octaethylporphyn (OEP) and quinone molecules dispersed in a polymeric matrix. It was observed a tendency in the phase behavior to small values only in the spectral region near to 620 nm, while for shorter wavelength did not show any tendency. These measurements suggested that the electron transfer to acceptor occurred with the participation of octaethylporphyn singlet excited state.

KEYWORDS: Electron transfer; photoacoustic spectroscopy; phase; acceptor; donor; polymer.

Introduction

The electron transfer process may proceed with the participation of any donor excited state to a non-excited acceptor state. At the present work the investigation of the electron transfer mechanism between octaethyl-porphyn (OEP) and Duroquinone (DQ) or dichloro-dicyano-benzoquinone (DDQ) using a photocalorimetric method was performed. The goal of this paper is to determine which excited state of the donor is involved in this process, the electron acceptor affinity, and what spectral region favors this process, which represents an electronic gate for the system. The calorimetric method¹ based on the photoacoustic effect⁷ (PAS) was applied during the investigation, this method is understood as follow. A system of absorbing molecules is exposed to an intensity-modulated monochromatic light, which produces a population of excited electronic states being also modulated. The decayments may happen by radiative and non-radiative routes, the second type constitutes the heat source for the photoacoustic effect. In an actual photoacoustic measurement many of the non-sample related parameters may be maintained constant and the phase data may therefore be used to provide information about the optical and thermal properties of the solid under study and besides that in the case where chemical reactions onset by light are present, the phase data

hold some aspects of the process. The use of PAS angle phase to investigate nonradiative deexcitation paths has been employed by Merkle & Powell.⁸ These authors took the relationship between nonradiative decayment and the phase shift previously used for gases by Robin⁵ and applied to solid material. Herein a new use of the phase shift is attributed to the electron transfer process, determining the participation of the donor excited state and the acceptor affinity as well as the the favorable spectral region.

Materials and methods

Sample preparation

Photoinduced electron transfer can be described most simply as the movement of an electron, caused by the absorption of light, from an electron rich species (a donor, OEP) to an electron deficient species (an acceptor, DQ and DDQ). The samples were prepared with a fixed concentration (1.4×10^{-4} M) of OEP from Sigma and different amounts (10, 20 and 40 times larger than OEP concentration) of DQ and DDQ, also from Sigma. They were dissolved in toluene and mixed with poly(methyl-methacrylate) and the resulting mixture was spread on a clean glass plate and extended to form films about 100 m m thick. As in the photoacoustic cell the volume of the sample influences the signal amplitude the thickness of the film were controlled through micrometer measurements and any film that exceeded to less or more than 100 m m of thickness was cast off. The DQ concentration films was calculated as the number of molecules per cubic angstrom. This was done considering the mass of DQ used, its molecular weight and the volume of film, obtained from mass and density (1.19 g/cm^3)¹¹ of the polymer. The films were left in the dark in a glove box filled with N_2 gas for about 12h. For each film, 3 to 4 pieces were measured and the averaged was considered in calculations. This procedure was applied to improve the signal-to-noise ratio and also to verify the homogeneity of the films.

In-phase and quadrature measurements

The one-dimensional model employed to determine the amplitude and phase of the photoacoustic signal is that developed by Rosencwaig & Gersho.¹⁰ The variable component of the phase of the photoacoustic signal may be derived from this complex quantity:

$$Q = Q_1 + iQ_2 = q \cdot \exp(-iq) \quad (1)$$

where Q is the photoacoustic amplitude, Q_1 is the in-phase amplitude measurement and Q_2 is the quadrature amplitude measurement, both obtained through the lock-in amplifier, and hence the phase is

$$q = \text{tg}^{-1}[-(Q_2/Q_1)] \quad (2)$$

where q is measured in degree.

The photoacoustic pressure pulses may be represented by the phase angle. These pulses generated from solid samples are caused by the transfer of heat from the sample surface to the air in the PAS cell and their values are delayed in relation to the lock-in reference angle. This happens because the

detection of the pulse follows the excitaton of the solid sample by a modulated light.

Results and discussion

To verify how the acceptor concentration increment influences the photoacoustic phase angle, measurements were carried out at the following bands 489, 534, 567 and 620 nm, which are the octaethylporphyn (OEP) absorbance peaks, [Figure 1 a, b](#). Since the maximum amplitude signal were in these peaks, we used them to avoid phase fluctuations what should mask the electron transfer effect. For each film, three pieces were measured and averaged. This procedure was used to confirm the random distribution of donor and acceptor molecules as well as the homogeneity of the drying process. The phase data contains contributions from a number of sources non-associated with the sample like, the geometry of the photoacoustic cell, the response of the detecting system, etc. As in the present work non-sample related parameters were maintained constant the phase data may therefore be used to provide information about the photoinduced electron transfer process. The phase angle was measured in relation to the lock-in reference angle always kept in 0° . The averaged phase responses with the increase of the acceptor concentrations at the bands 489, 534 and 567 nm were almost constant $-171.3^\circ \pm 1.7$, as shown in [Figure 2 a, b, c](#) respectively, and following the same procedure the phase behavior at 620 nm was remarkable, as shown in [Figure 3](#).

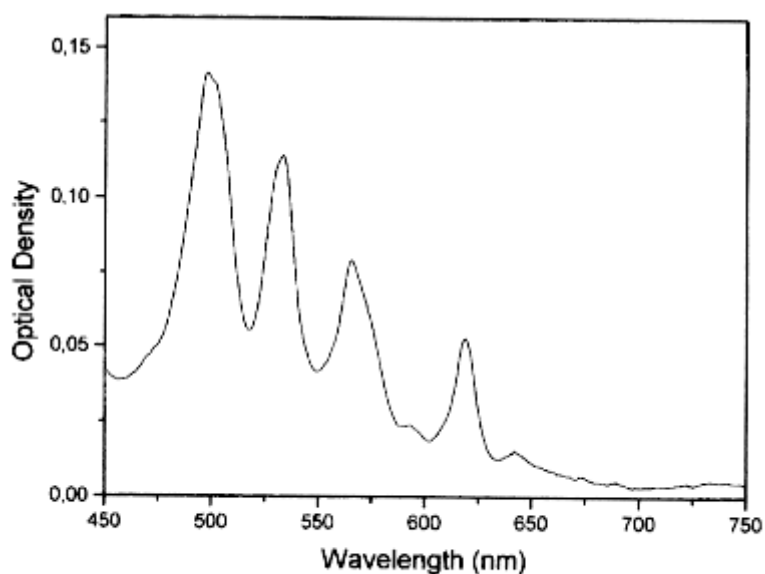


FIGURE 1 a - Optical absorption spectrum of OEP in toluene.

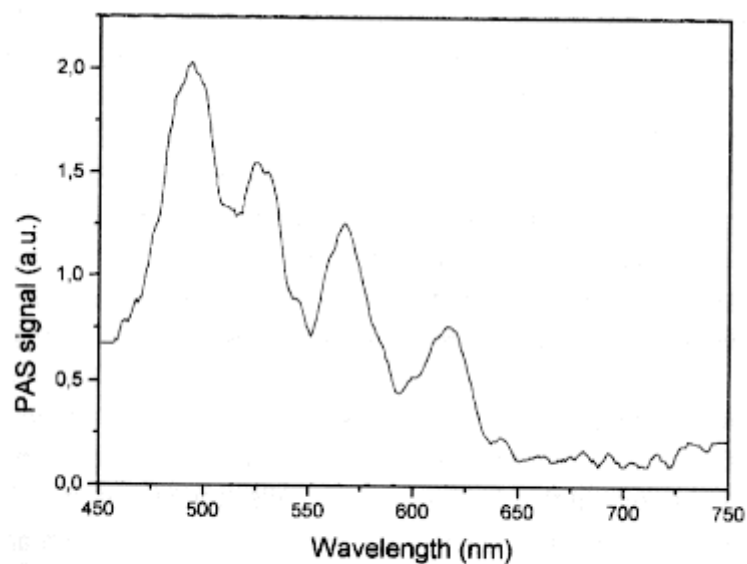


FIGURE 1 b - Photoacoustic spectrum of OEP with the concentration of $1.4 \times 10^{-4} \text{ M}$, obtained at 5 Hz.

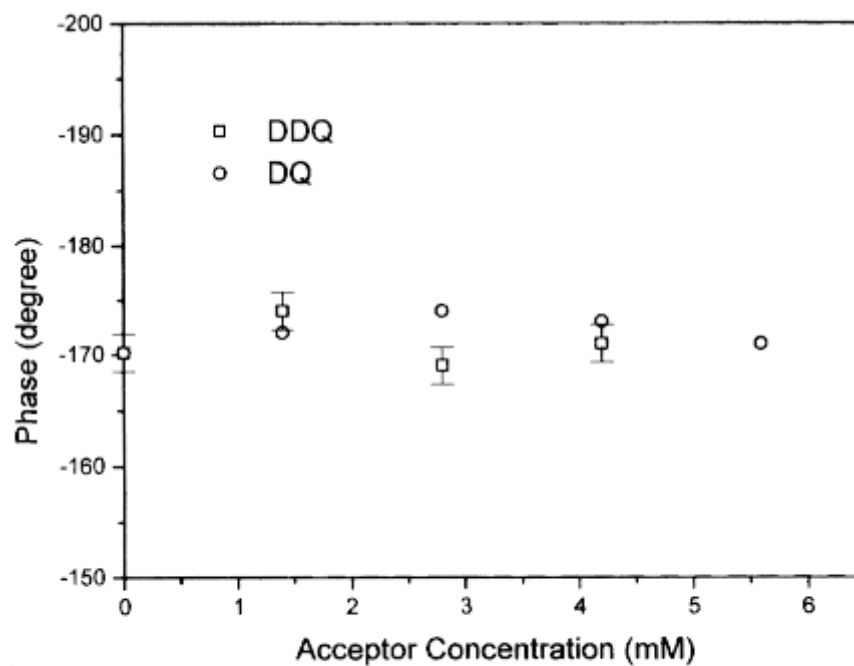


FIGURE 2 a - Phase angle times acceptor concentration DQ(○) and DDQ(□) at 498 nm and 5 Hz.

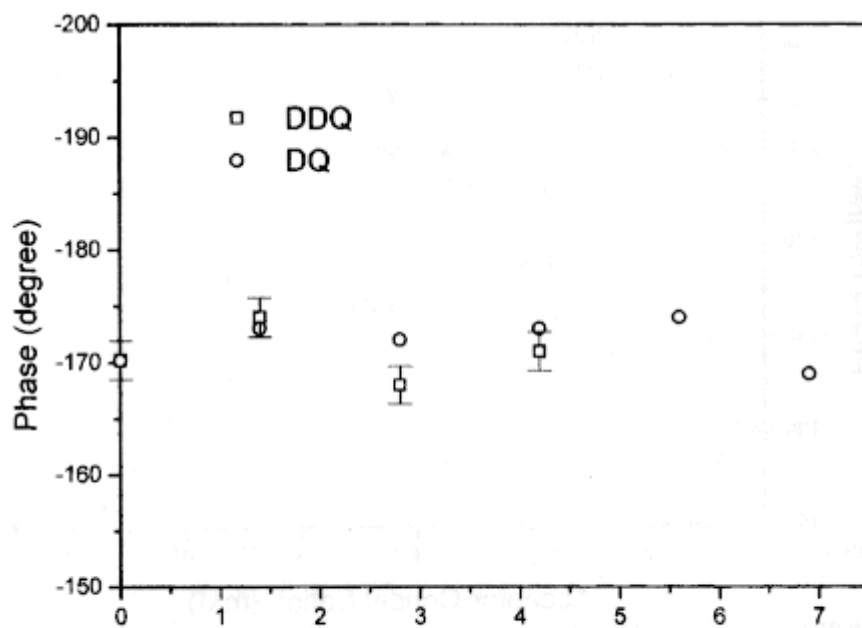


FIGURE 2 b - Phase angle times acceptor concentration DQ(○) and DDQ(□) at 534 nm and 5 Hz.

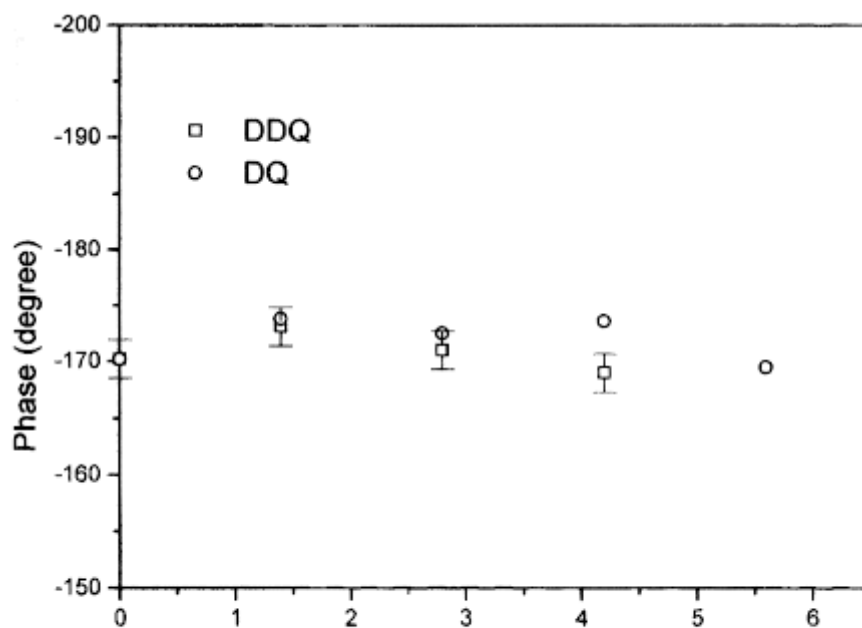


FIGURE 2 c - Phase angle times acceptor concentration DQ(○) and DDQ(□) at 567 nm and 5 Hz.

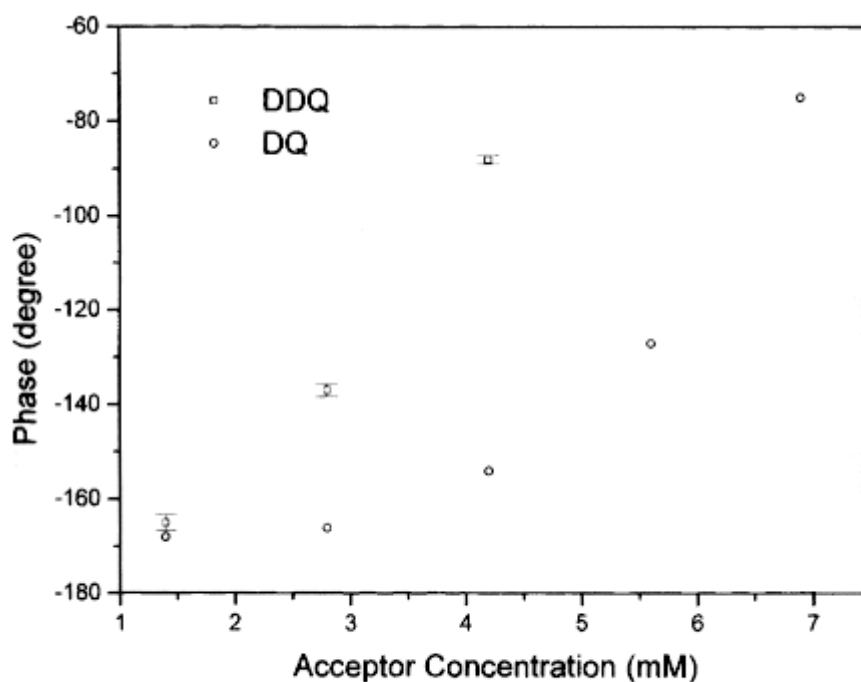


FIGURE 3 - Phase angle times acceptor concentration DQ(○) and DDQ(□) at 620 nm and 5Hz.

To have a better idea of what is happening, the angle of phase may be understood as the time lag between excitation and detection by the microphone and expressed as equation 2. The detector is really distinguishing a modification on the pressure pulse inside the photoacoustic cell, indicated by [Figure 3](#). Such changes has two mainly sources: an increase at the pressure amplitude and/or an increase at the pressure pulse velocity generation. The former was well established in a previous article² and the later is the object of this discussion.

On increasing the acceptor concentration electron transfer rate increases too, as a result, an induced phase shift is expected. If to smaller or higher values than that obtained for the films with donor molecules it depends only on the internal conversion efficiency of the acceptor molecules. Analyzing the phase behavior at 620 nm it indicates that the acceptor internal conversion must be higher than the donor molecules, considering that the electron transfer rate increases with the acceptor concentration, even though not being possible to differentiate this effect due to the low modulation frequency, after transferring the electron to the acceptor its decaysments by internal conversion is expected to be higher than the internal conversion of the donor molecule. This explanation encountered base from the current literature which is found that internal conversion quantum yields for benzoquinones derivatives are thousands times higher than porphyrins derivatives,¹² what explains the phase shift to smaller values indicating that non-radiative relaxation process became faster with the presence of the acceptor. It also suggests that the increment of the acceptor concentration affected the heat production responsible for the pressure variation in the photoacoustic cell, shortening the generation of the pressure pulse inside the cell. As this effect was only observed at 620 nm band it infers that the participation of the donor in the electron transfer process was performed by its singlet excited state.

The first detailed mechanism of electron transfer reaction with metalloporphyrins (MP) in vitreous

matrix dealt with the separation of charge of zinc and magnesium porphyrins in ethanol containing some addition of CCl_4 at 77 K.⁶ In these studies the electron transfer to the acceptor is shown to proceed from singlet excited states of MP.

Distinguishing the phase behavior difference between the first three bands, which shown to be constant and the band at 620 nm that showed a smoothed phase variation. It can also be explained considering that the decayments of the highest excited states happens to the first singlet excited state and from this backing to the ground state, via: luminescence and non-radiative decay. When acceptor molecules are present in the films, the electron can be transferred from donor to the acceptor, and this process becomes a new pathway for non-radiative decays, resulting in a large phase shift. And the electronic gate for the electron transport from donor to acceptor is identified and matches with the singlet excited state of OEP, that is in agreement with the result obtained by fluorescence technique³ and in agreement with Kasha's rule.⁴

The phase shift can also be used to distinguish the best capturing electron acceptor. Comparing the angle (Figure 3) values at the same concentration, it suggests that DDQ has a higher capturing efficiency action than DQ. As a result, it can be observed that DQ needs a higher concentration level in order to have similar capturing efficiency action as DDQ, and is known that DDQ has a larger electron affinity than DQ.⁹

Photoacoustic phase analyzes in this case represents an alternative way for distinguishing the electron affinity in a rigid medium. This measurement can be used to confirm the result obtained in electrochemistry when the donor-acceptor moyet is changed and if their properties are hold or not. In conclusion, the use of this photocalorimetric method to analyze the electron transfer process brought a new insight of the reactions involved in this process in a rigid medium.

CORNÉLIO, M. L. Transferência de elétrons via estado singleto excitado de porfírina de base livre e afinidade de elétrons por aceitadores em meio rígido análise fotoacústica do ângulo de fase. *Ecl. Quím. (São Paulo)*, v.22, p.83-92, 1997.

RESUMO: A espectroscopia fotoacústica obtém informações sobre amplitude e fase, da resposta de um sistema submetido a excitação por luz. Este artigo apresenta estudos do ângulo de fase no processo de transfereência de elétrons entre octaetilporfírina (OEP) e derivados de quinona ambos dispersos em uma matriz polimérica. Observou-se uma tendência no comportamento da fase para valores menores na região espectral próximo de 620 nm. Enquanto que para comprimentos de onda menores este efeito não foi apresentado. Estas medidas sugerem que a transferência de elétrons para o aceitador ocorreu com a participação do estado singleto excitado da octaetilporfírina.
PALAVRAS-CHAVE: Transferência de elétrons; espectroscopia fotoacústica; fase; aceitador; doador; polímero.

References

- 1 CALLIS, J. The calorimetric detection of excited states. *J. Res. Natl. Stand. Sect. A* . v.80A, p.413-19, 1976. [[Links](#)]
- 2 CORNELIO, M.L., SANCHES, R., Monitoring electron transfer by photoacoustic spectroscopy. *European Biophysics Journal*, v.23, n. 6, p.439-42, 1995. [[Links](#)]
- 3 _____. The use of photoacoustic spectroscopy to determine the critical distance for electron transfer. *J. Biochem. Biophys. Methods*. v.29, p.149-55, 1994. [[Links](#)]
- 4 KASHA, M. *Discuss. Faraday Soc.* v.9, p.14-9, 1950. [[Links](#)]
- 5 HARSHBARGER, W. R., ROBIN, M. B. *Acco. Chem Res.* v.6, p.329, 1973 [[Links](#)]
- 6 KHOLMOGOROV, V.E., BOBROSVSKII, A.P. *Problems of Biophotochemistry*. Moscow: Nauka, 1973. [[Links](#)]
- 7 McDONALD, F., WETSEL, G. Generalized theory of the photoacoustic effect. *J. Appl. Phys.* v.49, p.2313-22, 1978. [[Links](#)]
- 8 MERKLE, L. D., POWELL, R. C. *J. Phys. C*, v.11, p.303, 1977. [[Links](#)]
- 9 MILLER, J.R., BEITZ, J.V. Exothermic rate restriction on electron transfer in a rigid medium. *J. Chem. Phys.* v.71, p. 4579, 1979. [[Links](#)]
- 10 ROSENCWAIG, A., GERSHO, A. Theory of the photoacoustic effect with solids. *J. Appl. Phys.* v.47, p.64-9, 1976. [[Links](#)]
- 11 SCAIANO, J.C. (Ed.) *CRC Handbook of Organic Photochemistry*, Boca Raton, CRC Press, 1989. vol. 1, p.328. [[Links](#)]
- 12 _____. (Ed.) *CRC Handbook of Organic Photochemistry*, Boca Raton, CRC Press, 1989. vol.2. [[Links](#)]

Recebido em 3.3.1997.

Aceito em 4.4.1997

* Departamento de Física - UNESP - São José do Rio Preto - 15054-000 - Brasil.